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Electronic Structures and Reaction Dynamics of Open-shell Species

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Editorial

Electronic Structures and Reaction Dynamics of Open-shell Species

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Communication

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Part III. Observation of intensity borrowing *via* ground state mixing

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On the vibronic level structure in the NO_3 radical

Part III.† Observation of intensity borrowing *via* ground state mixing

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The $\tilde{A}^2E'' \leftarrow \tilde{X}^2A'_2$ absorption spectrum exhibits vibronically allowed transitions from the ground state of NO_3 to upper state levels having a''_1 and e' vibronic symmetries. This paper explores the coupling mechanisms that lend intensities to these features. While transitions to e' vibronic levels borrow intensity from the very strong $\tilde{B}^2E' \leftarrow \tilde{X}^2A'_2$ electronic transition, those to a''_1 levels involve only negligible upper-state borrowing effects. Rather, it is the vibronic mixing of the *ground* vibronic level of NO_3 with vibrational levels in the $\tilde{B}^2E'$ electronic state that permit the a''_1 levels to be seen in the spectrum. These ideas are supported by vibronic coupling calculations. The fact that the intensities of features corresponding to the two different vibronic symmetries are comparable is thus accidental.

The nitrate radical (NO_3) has a rich spectroscopic history that began in nineteenth century Paris,[1] and the complex quantum mechanics that govern the behavior of this molecule continue to challenge latter-day experimentalists and theoreticians. Essentially all that is known about NO_3 from spectroscopy pertains to the three (or five, depending on perspective) lowest doublet electronic states: the ground $\tilde{X}^2A'_2$ state, and the two low-lying electronically degenerate states, $\tilde{A}^2E''$ and $\tilde{B}^2E'$, which are located approximately 7062 and 15 094 cm^{-1} above the ground state, respectively. The very strong X–B band system is well-known, and in fact was that observed in the ancient experiments carried out by Hautefeuille and Chappuis.[1] It continues to be the spectroscopic probe used by atmospheric chemists to measure the concentrations of NO_3, which is the principal oxidizing agent in the nighttime troposphere.[2] The principal complication in the understanding of NO_3 is that these five electronic states are heavily mixed by vibronic coupling.

The position of the $\tilde{A}^2E''$ state was not known with any certainty whatsoever until it was observed by electron photodetachment of the nitrate anion by Weaver *et al.* in 1991.[3] Optical characterization of this state is complicated because the X–A electronic transition is forbidden by dipole selection rules; indeed, the first observation of a vibronically allowed near-infrared transition at 7602 cm^{-1} was not reported by Hirota and coworkers until six years later.[4] In addition, the $\tilde{A}^2E''$ state is subject to the first-order Jahn–Teller effect, which distorts the equilibrium geometry from the idealized D_{3h} structure to a pair of three-fold equivalent C_{2v} geometries, which have $^2B_1$ and $^2A_2$ electronic symmetries. The former are minima on the adiabatic potential energy surface and the latter transition states for pseudorotational interconversion of the equivalent $^2B_1$ states.[5] There is a general consensus that the equilibrium geometry of the $^2B_1$ state has two short and one long NO bonds and an ONO (short–short) bond angle of about 130°, and that the pseudorotation barrier is in the range 1000–1500 cm^{-1}.[5,6] The spectroscopy of the $\tilde{A}^2E''$ state has rather recently been expanded significantly by the work in one of our laboratories, the preliminary analysis of which was reported in ref. 7. Additional data has been taken since that time, and will be documented and analyzed in a future publication. The point of this short report is to support the contention that an unusual intensity borrowing mechanism is operative in the vibronic X–A band system. While this mechanism was suggested in a previous paper,[6] numerical supporting evidence is presented here for the first time.

Electric dipole selection rules dictate that transitions from the a'_2 ground vibronic level of NO_3 are permitted to upper states of e' and a''_1 vibronic symmetries, which should give rise to perpendicular and parallel bands, respectively. The first two vibronic bands in the $\tilde{A}^2E''$ state (see Fig. 1) have the most certain assignments: 4_0^1 (a''_1 upper state vibronic symmetry) at 7602 cm^{-1}[4] and 2_0^1 (e' upper state vibronic symmetry) at 7744 cm^{-1}.[8] They have comparable band strengths in the observed spectrum. However, these two bands are parallel and perpendicular bands, respectively, and as we show, necessarily derive intensity from different mechanisms. The similarity in their observed intensities is therefore completely accidental.

The mechanism by which the e' vibronic levels gain intensity appears at first glance to be clear; it would seem to be a textbook example of intensity borrowing from the very strong X–B transition. Schematically, all e' levels nominally associated with the $\tilde{A}^2E''$ electronic state have wavefunctions of the Born–Huang form (using an electronically diabatic basis)

$$|\Psi_A\rangle = |\psi_A\Omega_{a''_2}\rangle + \lambda_{BA}|\psi_B 0_0\rangle + \cdots \quad (1)$$

where $\Omega_{a''_2}$ is the usual description of the vibrational mode ν_2 in the case of the 7744 cm^{-1} feature. λ_{BA} is the projection of

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† For Parts I and II see ref. 9.

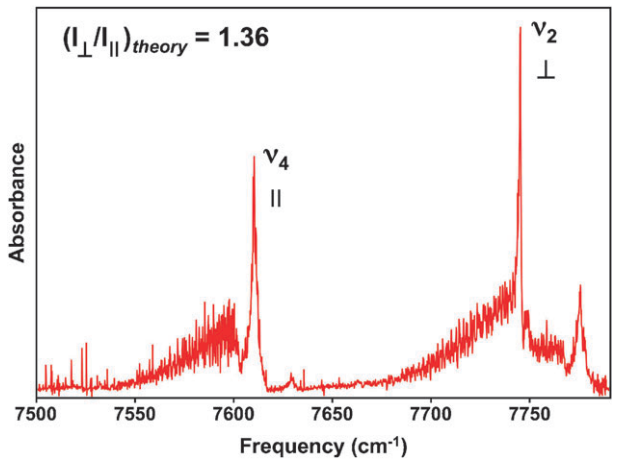

Fig. 1 Experimental cavity ringdown spectrum of the X–A band system of NO_3 in the region of the 2_0^1 and 4_0^1 bands. This spectrum is an expansion of the data shown in Deev *et al.*[7] Overlaid on the spectra are stick spectra calculated with the quasidiabatic basis discussed in the text.

the nuclear wavefunction associated with the B state diabatic electronic function—see Fig. 2—onto the ground vibrational

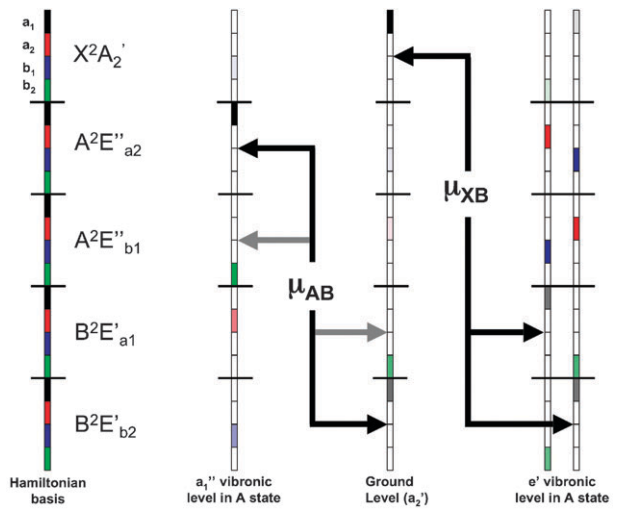

Fig. 2 Schematic intensity borrowing mechanisms for transitions from the ground (a'_2) vibronic level of NO_3 to the 4_1 and 2_1 levels of the $\tilde{A}^2E''$ state. Each column represents an eigenfunction. The basis of the quasidiabatic Hamiltonian is shown on the left-hand side, where the symmetries of the vibrational (nuclear) basis functions and each electronic basis function are symmetry-adapted to irreducible representations of the C_{2v} subgroup. Transitions are shown between the ground (a'_2) vibronic level (center) and nominal $\tilde{A}^2E''$ state levels with a''_1 vibronic symmetry (4_1, on right) and e′ vibronic symmetry (2_1, on left). Dark shading of the eigenvectors indicates the major components, while lighter shading indicates small eigenvector components. Unshaded regions are zero by symmetry. Allowed electric dipole moments are shown as arrows between the ground state and the $\tilde{A}$ state eigenvectors. The total transition moment is obtained from the electronic moment between different regions of the vector multiplied by the vibrational overlap integrals. The only nonvanishing contributions for both transitions are shown. Note that two overlap integrals contribute to each transition moment; each of these contributions is equal and carries the same sign.

level of the absorbing state (as given by the corresponding eigenvector of a quasidiabatic Hamiltonian.[9–11] The small contribution of the B state included above is responsible for the intensity since[12]

$$\begin{aligned}\langle\psi_X|\mu|\Psi_A\rangle &= \langle\psi_X|\mu|\psi_A\rangle\langle 0_0|\Omega_{a''_2}\rangle + \lambda_{BA}\langle\psi_X|\mu|\psi_B\rangle + \cdots \\ &= \lambda_{BA}\mu_{XB}. \end{aligned} \quad (2)$$

The vibronic coupling λ_{BA} between the A and B states is mediated by the a''_2 (umbrella) bending mode.

The source of intensity is much less obvious for transitions to the levels with a''_1 symmetry. Specifically, the calculations of Eisfeld and Morokuma have shown that there is no nearby $^2A''_1$ electronic state[5] for these levels to couple to and from which to borrow intensity. The nearest electronic state of this symmetry is some 8 eV above the $\tilde{A}^2E''$ [5] state, and is predicted to be quite dark spectroscopically,[13] which makes a similar upper state borrowing mechanism most unlikely. However, a rather unusual alternative also exists, which was mentioned as a possibility in ref. 6. That is, the *ground* electronic state in NO_3 is coupled quite strongly (*via* the ν_3 and ν_4 e′ modes) with the B state. Consequently, the ground vibronic level of this molecule can be viewed as undergoing the following sort of PJT mixing (as expressed in the Born–Huang basis)

$$|\Psi_X\rangle = |\psi_X 0_0\rangle + \sum_i \lambda_{XB}^{(i)}|\psi_B\Omega_{e'}^{(i)}\rangle + \cdots, \quad (3)$$

where the vibrational functions $\Omega_{e'}^{(i)}$ are those that project onto the e′ block of the nuclear component of wavefunctions corresponding nominally to vibrational levels in the $\tilde{B}^2E'$ state (see Fig. 2). The transition moment between the ground vibronic level and states such as the 4^1 A state level seen at 7602 cm^{-1} are then

$$\begin{aligned}&\langle\Psi_X|\mu|\psi_A\Omega_{e'}\rangle \\ &= \langle\psi_X|\mu|\psi_A\rangle\langle 0_0|\Omega_{e'}\rangle + \lambda_{XB}\langle\psi_B|\mu|\psi_A\rangle\langle\Omega_{e'}|\Omega_{e'}\rangle + \cdots \\ &= \lambda_{XB}\mu_{BA} \end{aligned} \quad (4)$$

where the leading term vanishes and the intensity comes from the second contribution. Note that while this treatment is similar to the ubiquitous upper state borrowing (in that the only difference is in the side of the integral which is expanded in the quasidiabatic basis) and is clearly valid from a quantum-mechanical point of view, the idea that a vibronic transition is lent intensity by mixing of the *ground* electronic state with another state is not particularly common in electronic spectroscopy. While the possibility that such a mechanism might be relevant was apparently first discussed by Orlandi and Siebrand[14,15] and postulated to be seen in pyrene,[15] we are unaware of any other compelling evidence to support such an idea in the literature.

The description above, which is an elaborated version of the argument given in ref. 6, has been studied numerically using the KDC Hamiltonian approach.[10] While details for NO_3 are given elsewhere,[9] this method uses a quasidiabatic representation of the electronic states (which is that used in all intensity borrowing arguements above) and a model vibronic Hamiltonian.[10] For the five state problem of NO_3, the vibronic basis set is illustrated schematically in Fig. 2 and described in the corresponding caption. Using this basis set, the states

corresponding to the 4_0^1 and 2_0^1 transitions were calculated with a direct product basis consisting of thirty basis functions for the degenerate ν_4 mode and ten functions for all other modes. The Hamiltonian, which will be described elsewhere, was parametrized using a quadratic Jahn–Teller treatment of the $\tilde{A}^2E''$ state and the equation-of-motion coupled-cluster approach EOMIP-CCSD.[11] The $\tilde{X}^2A'_2$ and $\tilde{B}^2E'$ state parametrizations were those of ref. 9 and 16. Electronic transition moments μ_{BX} and μ_{BA} were calculated with the EOMIP-CCSD method using the general approach described in ref. 17 with the natural orbital basis set of Taylor and Almlöf.[18]

The calculations show that the electronic moments of the two transitions, the 2_0^1 and 4_0^1 bands, differ by a factor of about five (with μ_{XB} larger),[19] which would suggest that the e′ features in the spectrum might dominate the a''_1 bands. However, the vibrational overlap integrals that appear in eqn (2) and (4) compensate for the intrinsically stronger X–B moment. The results of the calculation give a predicted intensity ratio for the two features of 1.36. The experimental ratio of the integrated intensities of the two bands (after accounting for a partially overlapping hot-band under the 2_0^1 band) is 1.8; thus the theoretical result is in good agreement with experiment (see Fig. 2).

The calculations confirm that the ground state mixing intensity-borrowing mechanism described above and in ref. 6 is responsible for the oscillator strength in the parallel bands in the X–A band system of NO_3. The similarity in the parallel and perpendicular band intensities is fortuitous, arising from mutually canceling strengths of the respective borrowed electronic transition moments and coupling terms. An accurate simulation of the complete spectrum, rather than just the lowest-energy vibronic level of each symmetry, requires a more elaborate Hamiltonian parametrization, a project that is currently under way in our laboratories.

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